

Description

Lubricating Oil Composition for Internal Combustion Engine

[Technical Field]

The present invention relates to lubricating oil compositions for internal combustion engines and particularly to those having excellent anti-wear properties, base number retaining properties, high-temperature detergency, and low friction characteristics.

[Background Art]

Zinc dialkyldithiophosphates (ZDTP) have excellent anti-wear properties and anti-oxidation properties as a peroxide decomposer and thus have been used as an essential additive in lubricating oils for internal combustion engines or in every sort of lubricating oils.

On the other hand, lubricating oil compositions blended with zinc dialkyldithiocarbamates and sulfur-based additives so as to retain the anti-wear properties are known as ZDTP-free lubricating oils as disclosed in Japanese Patent Laid-Open Publication Nos. 52-704, 62-253691, 63-304095, and 6-41568 and Published Japanese Translation Nos. 62-501572,

62-501917, and 1-500912. The lubricating oils disclosed in these publications contain a large quantity of sulfur similarly to those containing ZDTP. Such lubricating oils are poor in oxidation stability and tend to be acceleratingly decreased in base number.

After an extensive research and study, focusing on the ability to retain the base number of lubricating oils for internal combustion engine containing a large amount of sulfur, it was found that a compound containing sulfur such as ZDTP itself generates sulfuric acid in the lubricating oil when oxidized or thermally decomposed, and thus the lubricating oil containing such a compound is exhausted in base number, leading to a shortened working life, significantly deteriorated in detergency particularly at high temperature, and poor in low friction characteristics.

It was also found that when a deeply-desulfurized gas oil decreased in sulfur content to 50 ppm by mass or less, for a diesel engine equipped with DPF (diesel particulate filter); kerosene, gasoline, LPG, or natural gas, containing 50 ppm by mass or less of sulfur; or hydrogen, dimethylether, or alcohol, containing no sulfur is used as fuel, a lubricating engine oil is decreased in sulfuric acid contamination caused by sulfur in the fuel and thus prolonged in working life, compared with the case using a high sulfur content fuel.

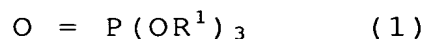
However, the use of such a low sulfur content fuel is too insufficient to provide an engine oil with a longer drain-interval and further enhance high-temperature detergency. Therefore, it is now necessary to study on an additive taking the place of various sulfur-containing anti-wear agents and anti-oxidants. Particularly, since gas engines are generally high in combustion temperature, the lubricating oil used therefor is exposed to high temperature or NOx and thus required to be improved in oxidation stability or high-temperature detergency. Furthermore, in order to maintain the performances of exhaust gas purifying systems such as DPF, ternary catalysts, oxidation catalysts, NOx adsorber catalysts, and EGR (exhaust gas recirculation) device, an engine oil is desired to be less in sulfur content.

Therefore, the object of the present invention is to provide a lubricating oil composition for internal combustion engines, which composition retains or is improved in anti-wear properties and anti-oxidation properties as obtained by conventional ZDTP; is enhanced in long-drain properties by decreasing the sulfur content of the oil so as to suppress the exhaust of the base number caused by deterioration of the oil; and is also excellent in high-temperature detergency and low friction characteristics.

[Disclosures of the Invention]

As a result of an extensive research and study, the present invention was completed based on the finding that a lubricating oil which is excellent in anti-wear properties, high-temperature detergency, and low friction characteristics and improved in base number retaining properties leading to long drain properties can be obtained by blending a lubricating base oil with a specific phosphorus compound, a specific ashless dispersant, a specific metal detergent, and a specific anti-oxidant, in a specific amount, respectively.

That is, according to the present invention, there is provided a lubricating oil composition for internal combustion engine, comprising a lubricating base oil; (A) a triphosphate represented by formula (1) below in an amount of 0.01 to 0.2 percent by mass in terms of phosphorus; (B) succinimide and/or derivative thereof in an amount of 0.01 to 0.3 percent by mass in terms of nitrogen; (C) an alkali metal or alkaline earth metal detergent in an amount of 0.05 to 1 percent by mass in terms of metal; and (D) a phenol-based and/or amine-based anti-oxidants in an amount of 0.01 to 3 percent by mass:



wherein the groups R^1 are each independently a

hydrocarbon group having 1 to 30 carbon atoms and may be the same or different from each other.

In the lubricating oil composition of the present invention, the alkali metal or alkaline earth metal detergent preferably contains an alkali metal or alkaline earth metal salicylate detergent.

In the lubricating oil composition of the present invention, the alkali metal or alkaline earth metal detergent is preferably an alkali metal or alkaline earth metal salicylate detergent whose metal ratio represented by "valence of metal element x metal element content (mol) / soap group content (mol)" is 3 or less.

In the lubricating oil composition of the present invention, the alkali metal or alkaline earth metal detergent is preferably a mixture of an alkali metal or alkaline earth metal salicylate detergent whose metal ratio represented by "valence of metal element x metal element content (mol) / soap group content (mol)" is 1.5 or less and an alkali metal or alkaline earth metal salicylate detergent whose metal ratio is more than 1.5.

In the lubricating oil composition of the present invention, the alkali metal or alkaline earth metal detergent is preferably a mixture of an alkali metal or alkaline earth metal salicylate detergent whose

metal ratio represented by "valence of metal element x metal element content (mol) / soap group content (mol)" is 1.5 or less and an alkali metal or alkaline earth metal sulfonate detergent.

The lubricating oil composition of the present invention preferably contains a sulfur-containing anti-wear agent in an amount of 0.1 percent by mass or less in terms of sulfur.

The lubricating oil composition of the present invention preferably contains a lubricating base oil whose aromatic content is 3 percent by mass or less and sulfur content is 50 ppm by mass or less.

The lubricating oil composition of the present invention is preferably used in an internal combustion engine using a fuel whose sulfur content is 50 ppm by mass or less.

The lubricating oil composition of the present invention is preferably used in gas engines.

The lubricating base oil of the lubricating oil composition of the present invention may be any of conventional mineral oils, synthetic oils, or mixtures of two or more of these oils mixed at an arbitrary ratio. For example, the mixture may be those of one or more types of mineral lubricating oils, those of one or more types of synthetic lubricating oils, or those of one or more types of mineral lubricating oils and one or

more types of synthetic lubricating oils.

Specific examples of mineral lubricating oils are paraffinic or naphthenic oils which can be obtained by subjecting a lubricating oil fraction produced by atmospheric- or vacuum-distilling a crude oil, to any one or more refining processes selected from solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, hydrorefining, washing with sulfuric acid, and clay treatment; and n-paraffines. Particularly, preferred are those obtained by a high-degree hydrocracking process or those obtained by isomerizing GTL Wax (Gas To Liquid Wax), both of which methods are capable of further decreasing the aromatic content and sulfur content.

No particular limitation is imposed on synthetic lubricating oils. Examples of synthetic lubricating oils include poly- α -olefins such as 1-octene oligomer, 1-decene oligomer, and ethylene-propylene oligomer, and hydrides thereof; isobutene oligomer and hydrides thereof; isoparaffines; alkylbenzenes; alkylnaphthalenes; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, and di-2-ethylhexyl cebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethyl hexanoate, and pentaerythritol pelargonate; polyoxyalkylene glycols;

dialkyldiphenyl ethers; and polyphenyl ethers.

No particular limitation is imposed on the sulfur content of the lubricating base oil. However, the sulfur content of the base lubricating oil is preferably 500 ppm by mass or less, more preferably 50 ppm by mass or less, even more preferably 20 ppm by mass or less, and particularly preferably 10 ppm by mass or less. A lubricating base oil containing too much sulfur would adversely affect the base number retaining properties of the resulting composition and the above-described exhaust gas purifying systems.

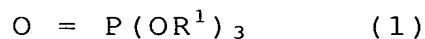
Although no particular limitation is imposed on the total aromatic content of the lubricating base oil, it is preferably 15 percent by mass or less, more preferably 10 percent by mass or less, and even more preferably 3 percent by mass or less, and particularly preferably 2 percent by mass or less. A lubricating base oil whose total aromatic content is more than 15 percent by mass would be poor in base number retaining properties and high-temperature detergency. The term "total aromatic content" used herein denotes an aromatic fraction content determined in accordance with ASTM D2549. The aromatic fraction includes alkylbenzenes; alkylnaphthalens; anthracene, phenanthrene, and alkylated products thereof; compounds wherein four or more benzene rings are condensated to each other; and compounds having

heteroaromatics such as pyridines, quinolines, phenols, and naphthols.

No particular limitation is imposed on the kinematic viscosity at 100 °C of the lubricating base oil. However, the kinematic viscosity at 100 °C is preferably 1 to 20 mm²/s and particularly preferably 2 to 10 mm²/s in order to improve low-temperature viscosity characteristics and oil film formation capability at lubricated sites and reduce the evaporation loss of the lubricating base oil.

No particular limitation is imposed on the viscosity index of the lubricating base oil. However, the viscosity index is preferably 80 or higher, more preferably 100 or higher, and further more preferably 120 or higher.

Component (A) of the lubricating oil composition of the present invention is a triphosphate represented by the formula



In formula (1), R¹ is a hydrocarbon group having 1 to 30 carbon atoms. Three groups of R¹ may be the same or different from each other.

Examples of the hydrocarbon group having 1 to 30 carbon atoms are alkyl, cycloalkyl, alkenyl, aryl, and arylalkyl groups.

Examples of the alkyl group include straight-chain or branched alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl groups.

The cycloalkyl group may have a substituent. Examples of the cycloalkyl group include those having 5 to 7 carbon atoms, such as cyclopentyl, cyclohexyl, and cycloheptyl groups; and alkylcycloalkyl groups having 6 to 11 carbon groups, such as methylcyclopentyl, dimethylcyclopentyl, methylethylcyclopentyl, diethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, methylethylcyclohexyl, diethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, methylethylcycloheptyl, and diethylcycloheptyl groups, of which the alkyl groups may bond to any position of the cycloalkyl groups.

Examples of the alkenyl group include those having 2 to 30 carbon atoms, such as butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, and octadecenyl groups, all of which may be straight-chain or branched and the position of which the double bonds may vary.

The aryl group may be substituted by an alkyl group. Examples of the aryl group include those having 6 to

18 carbon atoms, such as phenyl and naphthyl groups; and alkylaryl groups having 7 to 26 carbon atoms, such as tolyl, xylyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, dodecylphenyl, diethylphenyl, dibutylphenyl, and dioctylphenyl groups, wherein the alkyl groups may be straight-chain or branched and the position thereof to the aryl group may vary.

Examples of the arylalkyl groups include those having 7 to 12 carbon atoms, such as benzyl, phenylethyl, phenylpropyl, phenylbutyl, phenylpentyl, and phenylhexyl groups, of which the alkyl groups may be straight-chain or branched.

The hydrocarbon group of R^1 is preferably a straight-chain or branched alkyl group having 3 to 18 carbon atoms, an aryl having 6 to 18 carbon atoms, or a straight-chain or branched alkylaryl group having 7 to 26 carbon atoms, more preferably an alkyl group having 3 to 5 carbon atoms with the objective of excellent base number retaining properties, and is also preferably a straight-chain or branched alkyl group having 6 to 18 carbon atoms, an aryl having 6 to 10 carbon atoms, or a straight-chain or branched alkylaryl group having 7 to 10 carbon atoms with the objective of high-temperature detergency. In the present invention, R^1 is desirously a straight-chain or

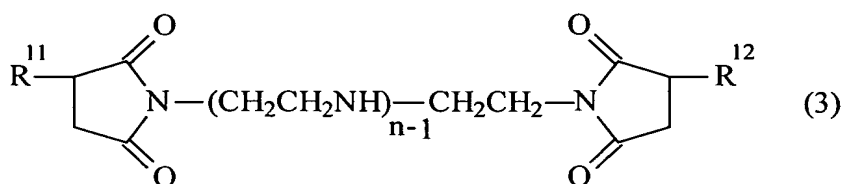
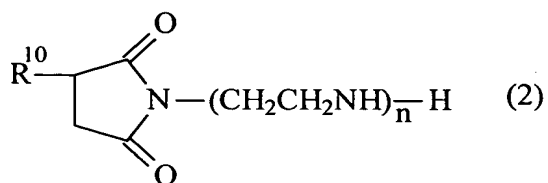
branched alkyl group having 6 to 18, preferably 6 to 12 carbon groups because the resulting composition would be low in volatility and excellent in high temperature detergency and friction-reducing effect. All the groups of R^1 are preferably the same.

The use of a triphosphate represented by formula (1) can decrease the metal content of the resulting composition compared with the use of a metal anti-wear agent such as ZDTP and can obtain a lubricating oil composition with more enhanced anti-wear properties, base number retaining properties, and high-temperature detergency, compared with the use of ZDTP, monophosphates, diesters, or phosphites.

The lower limit content of Component (A) is 0.01 percent by mass, preferably 0.02 percent by mass, and particularly preferably 0.05 percent by mass in terms of phosphorus, based on the total mass of the composition, while the upper limit content of Component (A) is 0.2 percent by mass, preferably 0.15 percent by mass, and particularly preferably 0.1 percent by mass in terms of phosphorus, based on the total mass of the composition. Component (A) of less than 0.01 percent by mass would fail to obtain advantageous effects of the present invention sufficiently, while Component (A) of more than 0.2 percent by mass would adversely affect exhaust gas purifying catalysts or the like.

Component (B) of the lubricating oil composition of the present invention is a succinimide and/or derivative thereof.

Examples of succinimide are monosuccinimides represented by formula (2) below and bissuccinimides represented by formula (3) below:



In formulas (2) and (3), R^{10} , R^{11} , and R^{12} are each independently a polybutenyl group and n is an integer of from 2 to 7. In the present invention, preferred are bis-type succinimides represented by formula (3) because they can further enhance the advantageous effects achieved by the present invention.

The polybutenyl group of R^{10} , R^{11} , and R^{12} has a number-average molecular weight of preferably 700 or greater, more preferably 900 or greater and preferably 3,500 or less, more preferably 2,500 or less, and particularly preferably 1,500 or less. A polybutenyl group having a number-average molecular weight of 700 or greater makes it possible to produce a lubricating oil composition with excellent detergent and

dispersion properties. Whereas, a polybutenyl group having a number-average molecular weight of 3,500 or less makes it possible to produce a lubricating oil composition with more excellent low-temperature flowability. With the objective of excellent advantageous effects of suppressing sludge formation, the lower limit of n is 2 and preferably 3, while the upper limit of n is 7 and preferably 6. The polybutenyl group can be obtained from polybutene (polyisobutene) produced by polymerizing a mixture of 1-buten and isobutene or a highly purified isobutene using a catalyst such as aluminum chloride or boron fluoride. The polybutene mixture contains polybutenes having a vinylidene structure at the terminal ends in an amount of generally 5 to 100 percent by mol. The polybutene (polyisobutene) may be those of which a slight amount of the remaining fluorine and chlorine resulting from the catalyst used in the process has been removed with a suitable treatment. Therefore, the content of halogen atoms such as fluorine and chlorine is preferably 50 ppm by mass or less, more preferably 10 ppm by mass or less, further more preferably 5 ppm by mass or less, and particularly preferably 1 ppm or less.

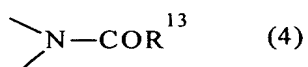
No particular limitation is imposed on the method of producing the succinimide represented by formula (2) or (3). For example, the succinimide may be produced by reacting a polybutenyl succinimide produced by

reacting polybutene obtained by chlorinating the above polybutene, preferably one from which chlorine and fluorine has been removed with maleic anhydride at a temperature of 100 to 200 °C, with polyamine such as diethylene triamine, triethylene tetramine, tetraethylene pentamine or pentaethylene hexamine. In the case of producing the bisuccinimide, the polybutenyl succinimide in an amount (molar ratio) of twice as much as polyamine may be reacted therewith, while in the case of producing the monosuccinimide, the polybutenyl succinimide in the same amount (molar ratio) may be reacted therewith.

The succinimide derivative may be a compound obtained by neutralizing or amidizing the whole or part of the remaining amino groups and/or imide groups by allowing a compound of formula (2) or (3) to react with an oxygen-containing organic compound or a boron compound.

Specific examples of the oxygen-containing organic compound include monocarboxylic acids having 1 to 30 carbon atoms, such as formic acid, acetic acid, glycolic acid, propionic acid, lactic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, oleic acid, nonadecanoic acid, and

eicosanoic acid; polycarboxylic acid having 2 to 30 carbon atoms, such as oxalic acid, phthalic acid, trimellitic acid, and pyromellitic acid, anhydrides thereof, and ester compounds thereof; alkyleneoxides having 2 to 6 carbon atoms, and hydroxy(poly)oxyalkylene carbonates. By allowing such oxygen-containing organic compounds to react as described above, the whole or part of the amino or imino group in the compound of formula (2) or (3) assumedly has a structure as represented by formula (4):



In formula (4), R^{13} is hydrogen, an alkyl, alkenyl or alkoxy group having 1 to 24 carbon atoms, or a hydroxy(poly)oxyalkylene group represented by $-\text{O}-(R^{14}\text{O})_m\text{H}$ wherein R^{14} is an alkylene group having 1 to 4 carbon atoms, and m is an integer of from 1 to 5.

Examples of the boron compound include boric acid, borates, and boric acid esters. Specific examples of boric acid include orthoboric acid, methaboric acid, and tetraboric acid. Examples of borates include alkali metal salts, alkaline earth metal salts, or ammonium salts, of boric acid. More specific examples include lithium borate such as lithium methaborate, lithium tetraborate, lithium pentaborate, and lithium perborate; sodium borate such as sodium methaborate, sodium diborate, sodium tetraborate, sodium

pentaborate, sodium hexaborate, and sodium octaborate; potassium borate such as potassium methaborate, potassium tetraborate, potassium pentaborate, potassium hexaborate, and potassium octaborate; calcium borate such as calcium methaborate, calcium diborate, tricalcium tetraborate, pentacalcium tetraborate, and calcium hexaborate; magnesium borate such as magnesium methaborate, magnesium diborate, trimagnesium tetraborate, pentamagnesium tetraborate, and magnesium hexaborate; and ammonium borate such as ammonium methaborate, ammonium tetraborate, ammonium pentaborate, and ammonium octaborate. Examples of the boric acid esters include esters of boric acid and an aliphatic alcohol having 1 to 6 carbon atoms and more specifically monomethyl borate, dimethyl borate, trimethyl borate, monoethyl borate, diethyl borate, triethyl borate, monopropyl borate, dipropyl borate, tripropyl borate, monobutyl borate, dibutyl borate, and tributyl borate.

No particular limitation is imposed on the mass ratio of boron and nitrogen (B/N ratio) in the succinimide reacted with a boron compound. However, the mass ratio is preferably from 0.1 to 1.2, more preferably from 0.2 to 1.0, and particularly preferably from 0.3 to 0.9 with the objective of enhancing the base number retaining properties and high-temperature detergency.

In the present invention, one or more selected from the above-described succinimides and derivatives thereof may be used as Component (B).

In the present invention, the lower limit content of Component (B) is 0.01 percent by mass, preferably 0.05 percent by mass, and particularly preferably 0.08 percent by mass in terms of nitrogen, based on the total mass of the composition. The upper limit content of Component (B) is 0.3 percent by mass, preferably 0.2 percent by mass, and particularly preferably 0.15 percent by mass in terms of nitrogen, based on the total mass of the composition. Component (B) of less than 0.01 percent by mass would fail to achieve the advantageous effect of the present invention, while Component (B) of more than 0.3 percent by mass would deteriorate the low-temperature viscosity characteristics and anti-emulsion properties of the resulting lubricating oil composition.

Component (C) of the lubricating oil composition of the present invention is an alkali metal or alkaline earth metal detergent. Component (C) include alkali metal or alkaline earth metal sulfonates, alkali metal or alkaline earth metal phenates, and alkali metal or alkaline earth metal salicylates. One or more alkali metal or alkaline earth metal detergents selected from the above compounds may be used, and particularly

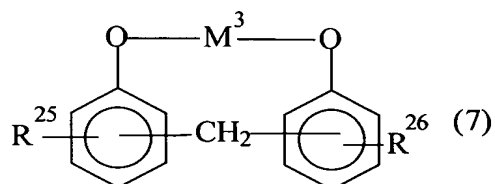
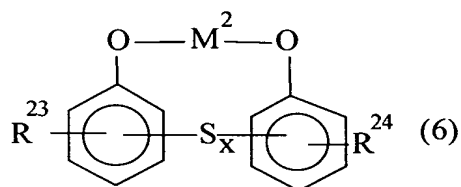
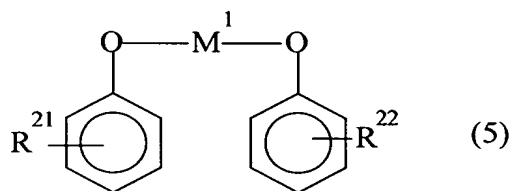
alkaline earth metal detergents are preferably used in the present invention.

Preferred alkaline earth metal sulfonates are alkaline earth metal salts, such as magnesium and/or calcium salts, preferably calcium salts, of alkyl aromatic sulfonic acids obtained by sulfonating alkyl aromatic compounds having a molecular weight of 300 to 1,500 and preferably 400 to 700.

Specific examples of the alkyl aromatic sulfonic acids include petroleum sulfonic acids and synthetic sulfonic acids.

Petroleum sulfonic acids may be those obtained by sulfonating alkyl aromatic compounds contained in the lubricant fraction of a mineral oil or mahogany acid by-produced upon production of white oil. The synthetic sulfonic acid may be those obtained by sulfonating an alkyl benzene having a straight-chain or branched alkyl group, by-produced from a plant for producing an alkyl benzene used as materials of detergents or obtained by alkylating an oligomer of an olefin having 2 to 12 carbon atoms such as ethylene and propylene to benzene or those obtained by sulfonating an alkylnaphthalene such as dinonylnaphthalene. Although not restricted, sulfonating agents used for sulfonating these alkyl aromatic compounds may be generally fuming sulfuric acids and sulfuric acid anhydride.

Examples of the alkaline earth metal phenates include alkaline earth metal salts, particularly magnesium salts and calcium salts of alkylphenols, alkylphenolsulfides or Mannich reaction products of alkylphenols. Specific examples are those represented by formulas (5) through (7):

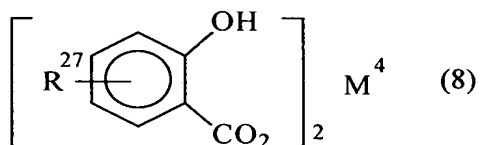


In formulas (5), (6), and (7), R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , and R^{26} may be the same or different from each other and are each independently a straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms, M^1 , M^2 , and M^3 are each independently an alkaline earth metal, preferably calcium and magnesium, and x is an integer of 1 or 2.

Specific examples of the alkyl group of R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , and R^{26} include butyl, pentyl, hexyl,

heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, and triacontyl groups. These alkyl groups may be straight-chain or branched and may be of primary, secondary, or tertiary.

Examples of the alkaline earth metal salicylates include alkaline earth metal salts, preferably magnesium and calcium salts, of an alkyl salicylic acid. Specific examples include compounds represented by formula (8)



In formula (8), R^{27} is a straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms and M^4 is an alkaline earth metal, preferably calcium or magnesium.

Specific examples of the alkyl group of R^{27} include butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, and triacontyl groups. These alkyl groups may be straight-chain or branched and may be of primary,

binary or tertiary.

The alkaline earth metal sulfonates, alkaline earth metal phenates, and alkaline earth metal salicylates may be (1) neutral (normal salt) alkaline earth metal sulfonates, neutral (normal salt) alkaline earth metal phenates, and neutral (normal salt) alkaline earth metal salicylates obtained by reacting alkyl aromatic sulfonic acids, alkylphenols, alkylphenolsuflides, Mannich reaction products of alkylphenol or alkyl salicylic acid as mentioned above directly with an alkaline earth metal base of the oxide or hydroxide of an alkaline earth metal such as magnesium and/or calcium or obtained by converting alkyl aromatic sulfonic acids, alkylphenols, alkylphenolsuflides, Mannich reaction products of alkylphenol or alkyl salicylic acid to an alkali metal salt such as sodium salt and potassium salt, followed by substitution with an alkaline earth metal salt; (2) basic alkaline earth metal sulfonates, basic alkaline earth metal phenates, and basic alkaline earth metal salicylates obtained by heating the neutral alkaline earth metal sulfonates, neutral alkaline earth metal phenates or neutral alkaline earth metal salicylates with an excess amount of an alkaline earth metal salt or alkaline earth metal base in the presence of water; and (3) overbased alkaline earth metal sulfonates, overbased alkaline earth metal phenates and overbased

alkaline earth metal salicylates obtained by reacting the hydroxide of an alkaline earth metal with carbonic acid gas or boric acid in the presence of the neutral alkaline earth metal sulfonates, neutral alkaline earth metal phenates or neutral alkaline earth metal salicylates.

The above-described neutral alkaline earth metal salts, basic alkaline earth metal salts, overbased alkaline earth metal salts, and mixtures thereof may be used in the present invention. Although not restricted, the base number of these compounds is generally 500 mgKOH/g or less, preferably from 60 mgKOH/g to 400 mgKOH/g. The term "base number" used herein denotes a base number measured by the perchloric acid potentiometric titration method in accordance with section 7 of JIS K2501 (1992) "Petroleum products and lubricants-Determination of neutralization number".

Although alkaline earth metal detergents are usually commercially available in the form of diluted with a light lubricating base oil, it is preferable to use metal detergents of which metal content is within the range of 1.0 to 20 percent by mass and preferably 2.0 to 16 percent by mass.

No particular limitation is imposed on the metal ratio of Component (C). However, it is preferable to use Component (C) whose metal ratio is generally 1 to

20, preferably 1 to 15.

In the present invention, Component (C) preferably contains the alkali metal or alkaline earth metal salicylate detergent as an essential component. The metal ratio of the detergent is preferably 3 or less, more preferably 2.6 or less, further more preferably 2 or less, and particularly preferably 1.5 or less. The alkali metal or alkaline earth metal salicylate detergent may be used singly or in the form of a mixture of those of different metal ratios. For example, an alkali metal or alkaline earth metal salicylate with a metal ratio of 2 or less, preferably 1.5 or less, and particularly preferably 1.2 or less may be used alone as an essential component. Alternatively, an alkali metal or alkaline earth metal salicylate with a metal ratio of 1.5 or less, preferably 1.2 or less may be used in combination with one with a metal ratio in excess of 1.5, particularly 2.6, and the metal ratio of the mixture is adjusted to 1.3 or more and preferably 2.3 or less, more preferably 2 or less, and particularly preferably 1.5 or less. Component (C) can enhance base number retaining properties, high-temperature detergency, and low friction characteristics by adjusting the metal ratio to be within the range of 1.3 to 2.3, even though the content of Component (C) is maintained the same.

Component (C) is preferably a combination of an

alkali metal or alkaline earth metal salicylate with a metal ratio of 1.5 or less, preferably 1.2 or less and an alkali metal or alkaline earth metal sulfonate. No particular limitation is imposed on the metal ratio of the alkali metal or alkaline earth metal sulfonate. However, the metal ratio is generally from 1 to 20, preferably from 1 to 15, and particularly preferably from 5 to 12. Component (C) thus prepared can further enhance advantageous effect to improve base number retaining properties, high-temperature detergency, and low friction characteristics.

The term "metal ratio" used herein is represented by "valence of metal element x metal element content (mol) / soap group (group such as alkylsalicylic acid group) content (mol)" and denotes the alkali metal or alkaline earth metal content against the content of the alkylsalicylic acid and alkylsulfonic acid groups in an alkali metal or alkaline earth metal detergent.

The lower limit content of Component (C) is 0.05 percent by mass, preferably 0.1 percent by mass, more preferably 0.15 percent by mass, and particularly preferably 0.2 percent by mass in terms of alkali metal or alkaline earth metal, based on the total mass of the lubricating oil composition of the present invention. The upper limit content of Component (C) is 1 percent by mass, preferably 0.5 percent by mass, and more preferably 0.4 percent by mass in terms of alkali metal

or alkaline earth metal, based on the total mass of the lubricating oil composition of the present invention. Component (C) of less than 0.05 percent by mass would fail to exhibit excellent base number retaining properties and high-temperature detergency, while Component (C) of more than 1 percent by mass would fail to attain effects as expected.

Component (D) of the lubricating oil composition of the present invention is a phenol- and/or amine-based anti-oxidant.

Examples of the phenol-based anti-oxidant include 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert- α -dimethylamino-p-cresol, 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol),

4,4'-thiobis(2-methyl-6-tert-butylphenol),
4,4'-thiobis(3-methyl-6-tert-butylphenol),
2,2'-thiobis(4-methyl-6-tert-butylphenol),
bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide,
bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide,
2,2'-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate],
tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)
propionate,
pentaerythrityl-tetraquis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate],
octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)
propionate,
octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)
propionate, and
octyl-3-(3-methyl-5-tert-butyl-4-hydroxyphenyl)
propionate. Two or more of these phenol-based
anti-oxidants may be used in combination.

Specific examples of the amine-based anti-oxidant include phenyl- α -naphthylamine, alkylphenyl- α -naphthylamine, and dialkyldiphenylamine. Two or more of these amine-based anti-oxidants may be used in combination. The above alkyl groups are those having 1 to 16 carbon atoms.

The above-described phenol-based and amine-based anti-oxidants may be used singly but preferably used in combination because the advantageous effects can be

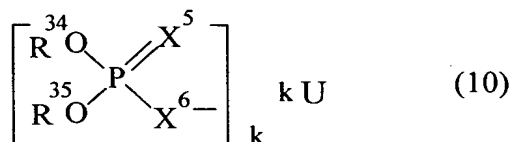
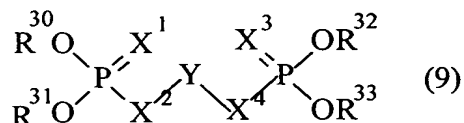
further enhanced.

The lower limit content of Component (D) is 0.01 percent by mass, preferably 0.1 percent by mass, more preferably 0.5 percent by mass, and particularly preferably 1.0 percent by mass, based on the total mass of the lubricating oil composition of the present invention with the objective of further enhancing the base number retaining properties and high-temperature detergency. The upper limit content of Component (D) is 3.0 percent by mass and preferably 2.5 percent by mass, based on the total mass of the lubricating oil composition of the present invention. Component (D) of more than 3.0 percent by mass would fail to attain sufficient anti-oxidant properties as balanced with the content.

The lubricating oil composition of the present invention may contain an anti-wear agent other than Component (A).

Examples of an anti-wear agent other than Component (A) include phosphorus- and/or sulfur-containing anti-wear agents such as thiophosphates and metal salts of phosphates, represented by formula (9) and thiophosphates, phosphates, and metal salts and amine salts thereof, represented by formula (10) and further include those such as phosphites, thiophosphites, and metal salts and amine salts thereof, thiotriphosphates, zinc

dialkyldithiophosphates, zinc
dialkyldithiocarbamates, molybdenum
dialkyldithiophosphates, molybdenum
dialkyldithiocarbamates, disulfides, olefin sulfides,
and sulfurized fats and oils:



In formulas (9) and (10), R^{30} , R^{31} , R^{32} , R^{33} , R^{34} , and R^{35} are each independently hydrogen or a hydrocarbon group having 1 to 30 carbon atoms. Examples and preferred examples of the hydrocarbon group having 1 to 30 carbon atoms include the same as those exemplified with respect to R^1 in formula (1) representing Compound (A) described above.

X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 are each independently oxygen or sulfur, at least one of them is oxygen, and preferably two or more of them are oxygen, and particularly preferably all of them are oxygen. Due to the presence of at least one oxygen, the resulting composition can be decreased in sulfur content and in the amount of sulfuric acid produced when being oxidized or thermally decomposed and thus can be significantly suppressed in the exhaust of the base

number.

Y is a metal atom and specifically zinc, copper, iron, lead, nickel, silver, and manganese. With the objective of enhanced anti-wear properties, Y is preferably zinc.

U is hydrogen (proton), a monovalent metal ion, or an ammonium ion. k indicates the number of ion of U and is an integer of from 1 to 20, preferably from 1 to 10, and more preferably from 1 to 8.

The monovalent metal ion of U is a metal atom which can form a salt and thus may be an alkali metal, such as lithium, sodium, potassium and cesium. The ammonium ion may be those providing ammonium ion such as nitrogen-containing compounds which can form an amine salt.

Examples of nitrogen-containing compounds include ammonia, monoamines, diamines, and polyamines. More specific examples include alkylamines having a straight-chain or branched alkyl group having 1 to 30 carbon atoms, such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine,

dioctylamine, dinonylamine, didecylamine, diundecylamine, didodecylamine, ditridecylamine, ditetradecylamine, dipentadecylamine, dihexadecylamine, diheptadecylamine, dioctadecylamine, methylethylamine, methylpropylamine, methylbutylamine, ethylpropylamine, ethylbutylamine, and propylbutylamine; alkenylamines having a straight-chain or branched alkenyl group having 2 to 30 carbon atoms, such as ethenylamine, propenylamine, butenylamine, octenylamine and oleylamine; alkanolamines having a straight-chain or branched alkanol group having 1 to 30 carbon atoms, such as methanolamine, ethanolamine, propanolamine, butanolamine, pentanolamine, hexanolamine, heptanolamine, octanolamine, nonanolamine, methanolethanolamine, methanolpropanolamine, methanolbutanolamine, ethanolpropanolamine, ethanolbutanolamine, and propanolbutanolamine; alkylenediamines having an alkylene group having 1 to 30 carbon atoms, such as methylenediamine, ethylenediamine, propylenediamine, and butylenediamine; polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine; heterocyclic compounds such as undecyldiethylamine, undecyldiethanolamine, dodecyldipropanolamine,

oleyldiethanolamine, oleylpropylenediamine, and stearyl tetraethylenepentamine, having an alkyl or alkenyl group having 8 to 20 carbon atoms bonded to the above-exemplified monoamines, diamines and polyamines and N-hydroxyethyl oleylimidazoline; alkylene oxide adducts thereof; and mixtures thereof.

In the case of using an anti-wear agent containing sulfur selected from the above anti-wear agents other than Component (A), no particular limitation is imposed on the content of the anti-wear agents. However, the content is preferably 0.1 percent by mass or less and more preferably 0.09 percent by mass or less in terms of sulfur, based on the total mass of the lubricating oil composition of the present invention. However, it is particularly preferable not to use the sulfur-containing anti-wear agent. A lubricating oil composition with significantly excellent base number retaining properties and high-temperature detergency can be obtained by decreasing the amount of the sulfur-containing anti-wear agent to 0.1 percent by mass or less.

In the case of blending a sulfur-free phosphorus-containing anti-wear agent selected from the above-described anti-wear agents other than Component (A), the content is from 0.01 to 0.2 percent by mass in terms of phosphorus, based on the total mass of the lubricating oil composition of the present

invention. Even in such a case, the total content of the anti-wear agent and Component (A) does not exceed preferably 0.2 percent by mass and particularly preferably 0.15 percent by mass in terms of phosphorus, based on the total mass of the composition because there is a risk that exhaust gas purifying catalysts are adversely affected.

Although the lubricating oil composition for internal combustion engines of the present invention is excellent in anti-wear properties, base number retaining properties, and high-temperature detergency, various additives may be optionally added in order to further improve these properties. Examples of such additives include viscosity index improvers, ashless dispersants other than Component (B), metal detergents other than Component (C), anti-oxidants other than Component (D), friction modifiers, corrosion inhibitors, rust preventives, anti-emulsifiers, metal deactivators, anti-foamers, and dyes.

Examples of viscosity index improvers include non-dispersion type viscosity index improvers such as copolymers of one or more monomers selected from various methacrylates or hydrides thereof; dispersion type viscosity index improvers such as copolymers of various methacrylates further containing nitrogen compounds; non-dispersion- or dispersion-type

ethylene- α -olefin copolymers of which the α -olefin may be propylene, 1-butene, or 1-pentene, or the hydrides thereof; polyisobutylenes or the hydrides thereof; styrene-diene hydrogenated copolymers; styrene-maleic anhydride ester copolymers; and polyalkylstyrenes.

It is necessary to select the molecular weight of these viscosity index improvers considering the shear stability thereof. Specifically, the number-average molecular weight of non-dispersion or dispersion type polymethacrylates is from 5,000 to 1,000,000 and preferably from 10,000 to 350,000. The number-average molecular weight of polyisobutylenes or hydrides thereof is from 800 to 5,000 and preferably from 1,000 to 4,000. The number-average molecular weight of ethylene- α -olefin copolymers and hydrides thereof is from 800 to 500,000 and preferably from 3,000 to 200,000.

Among these viscosity index improvers, the use of ethylene- α -olefin copolymers or hydrides thereof is contributive to production of a lubricating oil composition which is excellent particularly in shear stability. One or more compounds selected from the above-described viscosity index improvers may be blended in an arbitrary amount. The content of the viscosity index improvers is generally within the range of 0.1 to 20.0 percent by mass, based on the total mass

of the lubricating oil composition.

Examples of ashless dispersants other than Component (B) include benzylamines having in the molecules at least one alkyl or alkenyl group having 40 to 400 carbon atoms and derivatives thereof; and polyamines having in the molecules at least one alkyl or alkenyl group having 40 to 400 carbon atoms and derivatives thereof.

Examples of friction modifiers include aliphatic amines, fatty acids, fatty acid esters, and aliphatic alcohols, having an alkyl or alkenyl group having 6 to 30 carbon atoms.

Examples of corrosion inhibitors include benzotriazole-, tolyltriazole-, thiazole-, thiadiazole-, and imidazole-based compounds.

Examples of rust-preventives include petroleum sulfonates, alkylbenzene sulfonates, dinonylnaphthalenesulfonates, alkenyl succinic acid esters, and polyhydric alcohol esters.

Examples of anti-emulsifiers include polyalkylene glycol-based non-ionic surfactants such as polyoxyethylenealkyl ether, polyoxyethylenealkylphenyl ether, and polyoxyethylenealkylnaphthyl ether.

Examples of metal deactivators include imidazolines, pyrimidine derivatives, alkylthiadiazoles, mercaptobenzothiazoles,

benzotriazoles and derivatives thereof,
1,3,4-thiadiazolepolysulfide,
1,3,4-thiadiazolyl-2,5-bisdialkyldithiocarbamate,
2-(alkyldithio)benzoimidazole, and β
-(o-carboxybenzylthio)propionitrile.

Examples of anti-foamers include silicone,
fluorosilicone, and fluoroalkyl ether.

When these additives are added to the lubricating oil composition of the present invention, the content of each of the ashless dispersant other than Component (B), metal detergent other than Component (C), anti-oxidant other than Component (D), friction modifier, corrosion inhibitor, rust inhibitor, and anti-emulsifier is 0.01 to 5 percent by mass based on the total mass of the composition. The content of the metal deactivator is 0.005 to 1 percent by mass, while the content of the anti-foamer is 0.0005 to 1 percent by mass.

The lubricating oil composition of the present invention is preferably limited in the content of additive containing sulfur as well as the content of the above-described sulfur-containing anti-wear agent. The content of the sulfur-containing additive including the sulfur-containing anti-wear agent is preferably 0.1 percent by mass or less and more preferably 0.09 percent by mass or less based on the total mass of the composition. Particularly

preferably the lubricating oil composition contains no sulfur-containing additives including the sulfur-containing anti-wear agent. Although commercially available additives generally contain a solvent used when they are synthesized or a diluting oil such as a solvent-refined mineral oil used to improving the handleability of the additives, the term "sulfur-containing additives" used herein does not refer to sulfur compounds derived from such a solvent or diluting oil.

Even though the composition of the present invention contains sulfur originating from the solvent or diluting oil, the total sulfur content of the composition is 0.2 percent by mass or less, preferably 0.15 percent by mass or less, and particularly preferably 0.1 percent by mass or less. As a result, a composition which is excellent in anti-wear properties, base number retaining properties, and high-temperature detergency and capable of maintaining the performance of exhaust gas purifying catalysts can be obtained. In the present invention, a composition containing sulfur in an amount of 10 ppm by mass or less or containing substantially no sulfur can be obtained using a high-degree hydrocracked base oil whose content of sulfur originating from a solvent or diluting oil is 10 ppm by mass or less or a base oil produced by isomerizing GTL Wax (Gas To Liquid Wax) or a synthetic

oil, containing substantially no sulfur.

[Applicability in the Industry]

Even though the lubricating oil composition for internal combustion engines, of the present invention is decreased in the amount of a sulfur-containing agent such as ZDTP having both anti-wear and anti-oxidation properties or contains no such an agent at all, the composition is extremely improved in anti-oxidation properties and in base number retaining properties, i.e., long-drain properties, and also excellent in high-temperature detergency and low friction characteristics, but free from the decrease of anti-wear properties.

Furthermore, since the total sulfur content of the lubricating oil composition of the present invention can be held down and prevented from raising more than 0.2 percent by mass, the composition can suppress exhaust gas purifying catalysts from poisoning by sulfur and be used suitably for engines equipped with an exhaust-gas after-treatment device such as an exhaust gas purifying catalyst.

Moreover, the lubricating oil composition of the present invention can also be used suitably as lubricating oils required to have anti-wear properties, base number retaining properties, and high-temperature detergency, such as lubricating oils for driving means

such as automatic or manual transmissions; those for wet brakes; hydraulic oils; turbine oils; gear oils; and bearing oils.

[Best Mode for Carrying out the Invention]

Hereinafter, the present invention will be described in more details by way of the following examples and comparative examples, which should not be construed as limiting the scope of the invention.

(Examples 1 to 4 and Comparative Examples 1 and 2)

Lubricating oil compositions for internal combustion engines, each having the formulation and properties shown in Table 1 were prepared. The compositions containing 0.05 percent by mass of sulfur are those containing sulfur originating from the diluting oils contained in the additives.

The compositions of Examples 1 to 4 and Comparative Examples 1 and 2 were evaluated by the following performance characteristics evaluating tests.

(1) Changes in base number with time by ISOT

Each of the compositions was forced to deteriorate at a temperature of 165.5 °C in accordance with "Lubricating Oils for Internal Combustion

Engine-Determination of Oxidation Stability Test" (Indiana Stirring Oxidation Test (ISOT), JIS K 2514) and measured for change in base number (hydrochloric acid method) with time. The results are shown in Table 1. A higher base number remaining rate indicates that the composition was enhanced in base number retaining properties and thus found to be a long drain oil which was able to be used for a long period of time.

As shown in Table 1, the compositions of the present invention (Examples 1 to 4) were significantly higher in base number retaining properties than the compositions (Comparative Examples 1 and 2) containing ZDTP (sulfur-containing anti-wear agent) in such a general amount that they are used as lubricating oils for internal combustion engines, i.e., 0.16 percent by mass in terms of sulfur and 0.08 percent by mass in terms of phosphorus. The triphenylphosphate-containing compositions (Example 4) and particularly the tributylphosphate-containing composition (Example 3) were significantly higher in base number retaining properties than the trioctylphosphate-containing composition (Example 1).

(2) Changes in base number with time measured by a NO_x absorbing test

Each of the sample oils was forced to deteriorate by blowing thereto a NO_x gas under the conditions

(150 °C, NO_x : 1185 ppm) in compliance with those described in "Japanese Society of Tribologists Conference Preliminary Reports 1992, 10, 465" and measured for change in base number (hydrochloric acid method) with time. The results are shown in Table 1. A smaller reduction in base number indicates that the composition is enhanced in base number retaining properties even in the presence of NO_x as used in an internal combustion engine and is a long drain oil which can be used for a long period time.

As shown in Table 1, the compositions of the present invention (Examples 1 to 4) were found to exhibit excellent base number retaining properties and long drain properties under such an atmosphere that lubricating oils for internal combustion engines are exposed to NO_x, similarly to the results in the above-described ISOT.

(3) Anti-wear properties evaluated by FALEX test

The seizing load of each of sample pieces was measured by FALEX test in accordance with ASTM D3233 (A method, 290 rpm, room temperature). The results are shown in Table 1. The larger the seizing load, the composition exhibits more excellent anti-wear properties.

As shown in Table 1, the anti-wear properties of the compositions of the present invention were equal

to or higher than those of Comparative Examples 1 and 2.

(4) High-temperature detergency evaluated by a hot tube test

A hot tube test was conducted in accordance with JPI-5S-5599. The evaluation was made by grading the compositions as 10 points when they were colorless and transparent (no fouling) and those as 0 point when they were black and opaque. Between 10 and 0 point, evaluation was done using reference tubes which were made per grade beforehand. At 290 °C, 6 points or higher indicate that the oil composition has an excellent detergency for an ordinary gasoline or diesel engine. However, a lubricating oil composition for a gas engine preferably exhibits excellent detergency also at 300 °C or higher in this test.

It is confirmed from Table 1 that the compositions of the present invention exhibited extremely excellent high-temperature detergency even at a temperature of 300 °C or higher. Particularly, the composition containing trioctylphosphate which is conceivably lower in evaporation than tributylphosphate exhibited extremely excellent high-temperature detergency.

(Examples 5 to 9 and Comparative Example 3)

Lubricating oil compositions (Examples 5 to 9 and

Comparative Example 3) with the formulations and properties shown in Table 2 were prepared and evaluated by the following test. The results are shown in Table 2. The composition of Example 9 is the same as the one of Example 1 in Table 1, while the composition of Comparative Example 3 is the same as the one of Comparative Example 1 in Table 1.

(5) Low-friction characteristics evaluated by an LFW-1 boundary friction test

An LFW-1 boundary friction test was conducted at a load of 100 lbs, a temperature of 100 °C, and various speeds using an LFW-1 boundary friction tester.

As apparent from the results shown in Table 2, the composition of Example 9 (composition of Example 1 in Table 1) is also excellent in low friction characteristics, compared with the composition of Comparative Example 3 (composition of Comparative Example 1 in Table 1). The compositions containing a low metal ratio alkaline earth metal salicylate essentially as Component (C) (Examples 5 to 8) were found to exhibit extremely superior low friction characteristics. These compositions exhibited base number retaining properties, anti-wear properties, and high temperature detergency equally to or better than the composition of Example 9. Component (C) of the composition of Example 6 was a mixture of calcium

salicylate whose metal ratio is 1.0 and calcium salicylate whose metal ratio is 2.7, and the total metal ratio of Component (C) is 1.46. However, the composition of Example 6 contained less amount of Component (C) of Example 5 but was recognized to be decreased in friction coefficient particularly in the high velocity region synergistically, compared with the average between Examples 5 and 9 . In the case of using tributylphosphate or triphenylphosphate instead of trioctylphosphate as Component (A), the composition containing tributylphosphate or triphenylphosphate was superior in low friction characteristics to Comparative Example 3 but the composition containing trioctylphosphate exhibited the most excellent low friction characteristics.

The "mass %" in the tables is based on the total mass of the composition.

Table 1

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Base oil ¹⁾	balance	balance	balance	balance	balance	balance
(A) Tri(2-ethylhexyl)phosphate	0.08	0.05	0.08			
(A) Tributylphosphate						
(A) Triphenylphosphate				0.08		
(B) Polybutenyl succinimide ²⁾	0.10	0.10	0.10	0.10	0.10	0.10
(C) Alkaline earth metal detergent ³⁾	0.26	0.26	0.26	0.26	0.26	0.26
(D) Phenol-based anti-oxidant ⁴⁾	1.0	1.0	1.0	1.0	1.0	1.0
(D) Amine-based anti-oxidant ⁵⁾	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur-containing anti-wear agent A ⁶⁾		0.08			0.16	
Sulfur-containing anti-wear agent B ⁷⁾						0.16
Viscosity index improver ⁸⁾	5.0	5.0	5.0	5.0	5.0	5.0
Metal deactivator	0.05	0.05	0.05	0.05	0.05	0.05
Total content of sulfur-containing additive	0.00	0.08	0.00	0.00	0.16	0.16
Total sulfur content in composition	0.05	0.13	0.05	0.05	0.21	0.21
(1) Base number remaining rate (HCl method)	70	50	64	47	49	46
after 125 hours	38	27	41	29	15	23
after 192 hours	17	-	28	22	10	11
(2) Base number remaining rate (HCl method)	61	56	60	56	51	52
after Nox absorbing test	18	12	20	18	0	4
(3) Falex test	940	940	980	1030	900	940
290°C	10	10	10	10	10	10
300°C	10	8	10	10	7	7
310°C	8	2	2	5	1	1
320°C	1	1	1	1	0	0

1) high-degree hydrogenated mineral oil, kinematic viscosity: 5.6 mm²/s, aromatic content: 1.2 mass%, sulfur content: 10 mass ppm

2) bis type, number average molecular weight of polybutenyl group: 1,300, nitrogen content: 1.8 mass%

3) calcium salicylate, base number: 170 mgKOH/g, calcium content: 6.2 mass%

4) octyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, sulfur content: 0.0 mass%

5) alkylidiphenylamine (alkyl group: mixture of C₄ and C₈ alkyl groups)

6) zinc di(1,3-dimethylbutyl)dithiophosphate, sulfur content: 18.8 mass%, phosphorus content: 9.4 mass%

7) zinc di(2-ethylhexyl)dithiophosphate, sulfur content: 16.0 mass%, phosphorus content: 8.0 mass%

8) ethylene- α -olefin copolymer-based

Table 2

	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 3
Base oil ¹⁾	balance	balance	balance	balance	balance	balance
(A) Tri(2-ethylhexyl)phosphate	mass%	0.08	0.08	0.08	0.08	0.08
(B) Polybutenyl succinimide ²⁾	in terms of phosphorus	0.10	0.10	0.10	0.10	0.10
(C) Alkaline earth metal detergent ³⁾	in terms of nitrogen	0.26	0.13	0.13	0.26	0.26
(C) Alkaline earth metal detergent ⁴⁾	in terms of alkaline earth metal	0.13	0.13	0.13	0.13	0.13
(C) Alkaline earth metal detergent ⁵⁾	in terms of alkaline earth metal	0.13	0.13	0.13	0.13	0.13
(C) Alkaline earth metal detergent ⁶⁾	in terms of alkaline earth metal	0.13	0.13	0.13	0.13	0.13
(D) Phenol-based anti-oxidant ⁷⁾	mass%	1.0	1.0	1.0	1.0	1.0
(D) Amine-based anti-oxidant ⁸⁾	mass%	1.0	1.0	1.0	1.0	1.0
Viscosity index improver ⁹⁾	mass%	5.0	5.0	5.0	5.0	5.0
Metal deactivator	mass%	0.05	0.05	0.05	0.05	0.05
Sulfur-containing anti-wear agent A ¹⁰⁾	mass%	0.00	0.00	0.00	0.00	0.16
Total content of sulfur-containing additive	mass%	0.00	0.00	0.02	0.00	0.16
Total sulfur content in composition	mass%	0.05	0.05	0.07	0.05	0.21
LFW-1 boundary friction coefficient	slipping velocity 1,000mm/s	0.104	0.106	0.113	0.115	0.138
Load: 100 lbs	slipping velocity 750mm/s	0.106	0.110	0.115	0.118	0.141
Temperature: 100°C	slipping velocity 500mm/s	0.107	0.113	0.117	0.120	0.144
	slipping velocity 200mm/s	0.107	0.115	0.117	0.120	0.150
	slipping velocity 100mm/s	0.105	0.116	0.116	0.119	0.151
	slipping velocity 50mm/s	0.101	0.115	0.114	0.114	0.151

1) high-degree hydrogenated mineral oil, kinematic viscosity: 5.6 mm²/s, aromatic content: 1.2 mass%, sulfur content: 10 mass ppm

2) bis type, number average molecular weight of polybutenyl group: 1,300, nitrogen content: 1.8 mass%

3) calcium salicylate, base number: 70 mgKOH/g, calcium content: 2.3 mass%, metal ratio: 1.0

4) calcium salicylate, base number: 120 mgKOH/g, calcium content: 4.15 mass%, metal ratio: 1.8

5) calcium salicylate, base number: 170 mgKOH/g, calcium content: 6.2 mass%, metal ratio: 2.7

6) calcium sulfonate, base number: 300 mgKOH/g, calcium content: 12 mass%, sulfur content: 3.3 mass%, metal ratio: 10.0

7) octyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, sulfur content: 0.0 mass%

8) alkylidiphenylamine (alkyl group: mixture of C₄ and C₈ alkyl groups)

9) ethylene- α -olefin copolymer-based

10) zinc di(1,3-dimethylbutyl)dithiophosphate, sulfur content: 18.8 mass%, phosphorus content: 9.4 mass%